

Competitive Sorption of Phosphate and Calcium at the Gibbsite-Water Interface: A P-XANES Study

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Beamline(s) X19A

Introduction: As an important plant nutrient, phosphate is often applied as fertilizer in agriculture to ensure crop production. This has led to the accumulation of phosphate in agricultural soils. Furthermore, additions of animal waste have contributed to excessive levels of soil P in many parts of the USA, especially in the Mid-Atlantic region. These soils can act as non-point sources for phosphate via erosion and run-off, contributing to the nutrient-load in lakes, streams or estuaries. In fresh water, phosphate is the limiting nutrient for eutrophication to occur, causing deterioration of water quality and thus limiting water usage or threatening the safety of drinking water supplies. The mobility and availability of phosphate in most agricultural soils is determined by surface reactions with Fe and Al oxides and hydroxides. Due to the complexity of soil systems it is very likely that those surface reactions are influenced by the presence of a multitude of metal cations and organic and inorganic anions. Of interest is the effect that Ca can exert on phosphate reactions, since it is often applied in lime to raise the soil pH. A recent study (Rietra, Hiemstra et al. 2001) of the interaction between phosphate and Ca at the goethite surface showed that Ca is adsorbed at lower pH values in the presence of phosphate than it is in its absence while more phosphate is adsorbed at higher pH values in the presence of Ca. Although the concentrations of phosphate and calcium were kept below the solubility limit for apatite, the formation of a surface precipitate could not be excluded. P-XANES has proven to be an effective spectroscopic tool to distinguish between phosphate solids in diverse environments. Preliminary results of a study to distinguish between adsorption and surface precipitation in the system $\text{PO}_4\text{-Ca-Al(OH)}_3$ are presented.

Materials and Methods: Samples of co-adsorbed phosphate and Ca on gibbsite were prepared at pH 4 and 7. The gibbsite suspension ($\rho = 2.5 \text{ g/L}$), which was pre-equilibrated at the appropriate pH for 48 hours in a background electrolyte of 0.1 M NaCl, was spiked with a 50 mM CaCl_2 solution to give total concentrations of 0.5 mM or 0.13 mM and allowed to equilibrate for 10 seconds. It was then spiked with a 150 mM phosphate solution to give total concentrations of 0.75 mM or 0.15 mM and stirred for 24 hours while the pH was kept constant, first by means of an automated titrator, then by manual addition of small quantities of 0.1 M HCl. The solids were recovered by centrifugation, washed once with ethanol to remove entrained solution and freeze-dried. All P-XANES data were collected at beamline X-19A in fluorescence mode using a PIPS detector.

Results: The P-XANES spectra are shown below together with reference spectra of hydroxy-apatite and phosphate adsorbed to gibbsite. As the P concentration decreases at constant Ca concentration (decreasing P:Ca ratio), the peak at 2.166 keV becomes more prominent and a shoulder develops on the high-energy side of the white line. Both features appear as sharp peaks in the spectra of apatite and as more broad peaks in various calcium phosphate solids (data not shown). It can therefore be concluded that with decreasing P:Ca ratio a calcium phosphate precipitate is formed at the surface. This precipitation process has to be surface induced since the concentrations were well below the solubility limit of apatite.

Reference: Rietra, R. P. J. J., T. Hiemstra, et al. (2001). "Interaction between Calcium and Phosphate Adsorption on Goethite." *Environmental Science and Technology* **35**: 3369-3374.

